

APPENDIX D TO PART 63—ALTERNATIVE VALIDATION PROCEDURE FOR EPA WASTE AND WASTEWATER METHODS

1. Applicability

This procedure is to be applied exclusively to Environmental Protection Agency methods developed by the Office of Water and the Office of Solid Waste. Alternative methods developed by any other group or agency shall be validated according to the procedures in Sections 5.1 and 5.3 of Test Method 301, 40 CFR Part 63, Appendix A. For the purposes of this appendix, “waste” means waste and wastewater.

2. Procedure

This procedure shall be applied once for each waste matrix. Waste matrix in the context of this procedure refers to the target compound mixture in the waste as well as the formulation of the medium in which the target compounds are suspended. The owner or operator shall prepare a sampling plan. Wastewater samples shall be collected using sampling procedures which minimize loss of organic compounds during sample collection and analysis and maintain sample integrity. The sample plan shall include procedures for determining recovery efficiency of the relevant compounds regulated in the applicable subpart. An example of an acceptable sampling plan would be one that incorporates similar sampling and sample handling requirements to those of Method 25D of 40 CFR part 60, appendix A.

2.1. Sampling and Analysis

2.1.1. For each waste matrix, collect twice the number of samples required by the applicable regulation. Designate and label half the sample vials the “spiked” sample set, and the other half the “unspiked” sample set. Immediately before or immediately after sampling (immediately after in the context of this procedure means after placing the sample into the sample vial, but before the sample is capped, cooled, and shipped to the laboratory for analysis), inject, either individually or as a solution, all the target compounds into each spiked sample.

2.1.2. The mass of each spiked compound shall be 40 to 60 percent of the mass expected to be present in the

waste matrix. If the concentration of the target compounds in the waste are not known, the mass of each spiked compound shall be 40 to 60 percent of the limit allowed in the applicable regulation. Analyze both sets of samples (spiked and unspiked) with the chosen method.

3. Calculations

For each pair of spiked and unspiked samples, determine the fraction of spiked compound recovered (R) using the following equations.

where:

$m_r$  = mass spiked compound measured ( $\mu\text{g}$ ).

$m_s$  = total mass of compound measured in spiked sample ( $\mu\text{g}$ ).

$m_u$  = total mass of compound measured in unspiked sample ( $\mu\text{g}$ ).

where:

S = theoretical mass of compound spiked into spiked sample ( $\mu\text{g}$ ).

3.1. Method Evaluation

In order for the chosen method to be acceptable for a compound,  $0.70 \leq R \leq 1.30$  (R in this case is an average value of all the spiked and unspiked sample set R values). If the average R value does not meet this criterion for a target compound, the chosen method is not acceptable for that compound, and therefore another method shall be evaluated for acceptance (by repeating the procedures outlined above with another method).

3.2. Records and Reports

Report the average R value in the test report and correct all reported measurements made with the method with the calculated R value for that compound by using the following equation:

$$\text{ER01JY96.048}$$

3.3. Optional Correction Step

If the applicable regulation allows for correction of the mass of the compound in the waste by a published  $f_m$  value, multiply the reported result calculated above with the appropriate  $f_m$  value for that compound.

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